



OTTAWA HULL K1A 0G9

(11) (C) 1,338,095

(21) 599,593

(22) 1989/05/12

(45) 1996/02/27

(52) 402-1.5

BREVETS

MARQUES  
DE COMMERCE

DROITS  
D'AUTEUR

DESIGNS  
INDUSTRIELS

TOPOGRAPHIES  
DE CIRCUITS  
INTÉGRÉS

PATENTS

TRADE-MARKS

COPYRIGHT

INDUSTRIAL  
DESIGN

INTEGRATED  
CIRCUIT  
TOPOGRAPHY

(51) Int.Cl. <sup>6</sup> G03F 7/038

(19) (CA) **CANADIAN PATENT** (12)

(54) Photopolymerizable Composition

(72) Kawabata, Masami , Japan  
Harada, Masahiko , Japan  
Takimoto, Yasuyuki , Japan

(73) Nippon Paint Co., Ltd. , Japan

(30) (JP) Japan 117187/1988 1988/05/13

(57) 2 Claims

NO DRAWING



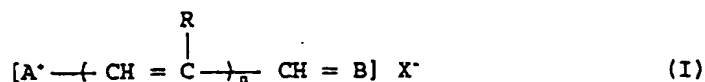
ABSTRACT

27 FEB. 1996

1338095

The present invention provides a photopolymerizable composition which is highly sensitive to visible light and near infrared rays, i.e. light of 600 to 900 nm, and has good stability over time. The photopolymerizable composition comprises a polymerizable compound having an ethylenically unsaturated double bond and a photopolymerization initiator wherein the photopolymerization initiator comprises;

(A) a cyanine dye having a peak absorption wavelength within 550 to 850 nm, represented by the formula;



wherein A and B respectively represent a substituted or unsubstituted nitrogen-containing heterocyclic ring and the nitrogen atom in the A ring has a positive charge, X<sup>-</sup> is a counter anion, R represents a hydrogen atom, an alkyl group having 1 to 3 carbon atoms, a phenyl group and a halogen atom, and n is an integer of 0 to 3; and

(B) a diaryliodonium salt.

1338095

PHOTOPOLYMERIZABLE COMPOSITION

The present invention relates to a photopolymerizable composition which is sensitive to visible light and near infrared rays.

5           As scanning exposure techniques with laser beams have progressed, many photopolymerizable compositions which are sensitive to visible light generated from an argon laser have been proposed.

10           However, semiconductor lasers have recently become noteworthy, because they do not require complicated equipment and are less expensive in comparison with gas lasers, e.g. argon lasers and helium-neon lasers. It has also been actively studied how the wavelength generated from semiconductor lasers changes from a near infrared  
15           range to a visible light range. It is considered possible that in the near future semiconductor lasers will practically generate visible light having a wavelength of 600 to 700 nm.

20           As a material which is sensitive to such visible light as well as near infrared rays, silver-salt photography and electrophotography are generally employed, but have drawbacks in coating workability, resolving power, etc.

It is also proposed that conventional

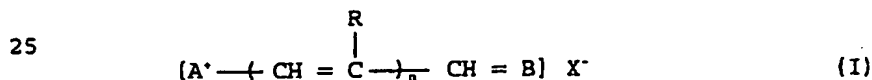


photopolymerizable compositions which are sensitive in a wavelength range less than about 500 nm are improved by replacing light absorbing components therein (e.g. dyestuffs) with those having a maximum absorption wavelength in a longer wavelength range of visible light. The proposed improvement does not always provide good properties. Some of the proposed compositions have insufficient sensitivity. If the compositions are sufficient in sensitivity, the sensitivity declines with time.

Accordingly, it is strongly desired to develop a photopolymerizable composition which is highly sensitive to a long wavelength range of visible light and a near infrared range and good storage stability over time.

The present invention provides a photopolymerizable composition which is highly sensitive to visible light and near infrared rays, i.e. light of 600 to 900 nm, and has good storage stability over time. The photopolymerizable composition comprises a polymerizable compound having an ethylenically unsaturated double bond and a photopolymerization initiator wherein the photopolymerization initiator comprises;

(A) a cyanine dye having a peak absorption wavelength within 550 to 850 nm, represented by the formula;



wherein A and B respectively represent a substituted or unsubstituted nitrogen-containing heterocyclic ring and the nitrogen atom in the A ring has a positive charge,  $X^-$  is a counter anion, R represents a hydrogen atom, an alkyl group having 1 to 3 carbon atoms, a phenyl group and a halogen atom, and n is an integer of 0 to 3; and

(B) a diaryliodonium salt.

The cyanine dye (A) contains a nitrogen-containing heterocyclic ring indicated A and B in the formula (I).

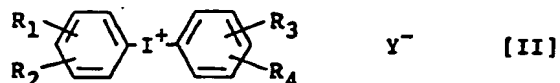
Typical examples of the heterocyclic rings are a pyridine ring, a quinoline ring, a thiazole ring, an oxazole ring, a benzothiazole ring, a benzoxazole ring, a benzoselenazole ring and the like. The heterocyclic ring may contain a substituent, e.g. a  $C_1-C_3$  alkyl group, a  $C_1-C_3$  alkenyl group, a phenyl group, a hydroxyl group, an amino group, a dialkyl ( $C_1-C_3$ ) amino group, a carboxyalkyl ( $C_1-C_3$ ) group, a sulphoalkyl ( $C_1-C_3$ ) group and a  $C_3-C_6$  esteralkyl group. The nitrogen atom in the ring A has a positive charge and  $X^-$  indicates a counter anion thereto. The counter anion  $X^-$  includes a halogen anion, e.g.  $Cl^-$ ,  $Br^-$ ,  $I^-$  and the like; an inorganic anion, e.g.  $BF_4^-$ ,  $Pf_6^-$ ,  $ClO_4^-$  and the like; and an organic anion, e.g.  $CH_3COO^-$ ,

$CH_3SO_3^-$ ,  $CH_3-C_6H_4-SO_3^-$  and the like.

Typical examples of the cyanine dyes in which the  $X^-$  anion is excluded are 3,3'-diethyl-2,2'-thiacarbocyanine, 3,3'-diethyl-9-phenyl-2,2'-thiacarbocyanine, 3,3'-diethyl-2,2'-(6,7,6',7'-dibenzo)thiacarbocyanine, 3,3'-diethyl-9,11-

neopentylene-2,2'-thiadibocyanine, 3,3'-diethyl-2,2'-  
 thiatricarbocyanine, 3,3'-diethyl-5,5'-dichloro-11-  
 diphenylamino-10,12-ethylenethiatricarbocyanine, 3,3'-di(3-  
 acetoxypropyl)-11-diphenylamino-10,12-ethylene-5,6,5',6'-  
 dibenzothiatricarbocyanine, 1,5-bis[3,4,5-trimethylthiazole-  
 5 (2)]pentamethinecyanine, 3,3'-diethyl-9-methyl-2,2'-  
 selenacarbocyanine, 3,3',9-trimethyl-2,2'-(4,5,4',5'-  
 dibenzo)thiacarbocyanine, anhydro-3,3'-dicarboxymethyl-2,2'-  
 thiacarbocyanine, 1,1'-diethyl-1,4,4'-quinocyanine, 1,1'-  
 diethyl-2,2'-quinocarbocyanine, 1,3'-diethyl-4,2'-  
 10 quinothiacarbocyanine, 1,1'-diethyl-4,4'-quinocarbocyanine,  
 1,1',3,3,3',3'-hexamethyl-2,2'-indotricarbocyanine, 2-[(3-  
 allyl-4-oxo-5-(3-n-propyl-5,6-dimethyl-2-benzothiazolidene)  
 methyl]-3-ethyl-4,5-diphenylthiazolinium, 2-(9-  
 acrydinylmethyl)-3-methylbenzothiazolium and the like.

15           The diaryliodonium salt (B) employed in the present  
 invention is generally represented by the formula [II];



wherein  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$ , which are the same or different,  
 20 represent a hydrogen atom, a halogen atom (e.g. chlorine and  
 bromine), an alkyl group which preferably has 1 to 4 carbon  
 atoms (e.g. methyl, ethyl, propyl and t-butyl), an alkoxy  
 which preferably has 1 to 3 carbon atoms (e.g. methoxy,  
 ethoxy and propoxy) and a nitro group,  $\text{Y}^-$  represents a  
 25 halogen ion (e.g.  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$ ), a hydroxyl ion,  
 $\text{HSO}_4^-$ ,  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ,  $\text{AsF}_6^-$  or  $\text{SbF}_6^-$ . Examples of the

diaryliodonium salts are-chloride, bromide,  
tetrafluoroborate, hexafluorophosphate, hexafluoroalcalenate  
and hexafluoroantimonate of iodonium moieties (e.g.  
diphenyliodonium, bis(p-chlorophenyl)iodonium,  
ditolyliodonium, bis(p-t-butylphenyl)iodonium and bis(m-  
5 nitrophenyl)iodonium).

The photopolymerizable composition of the present  
invention may be prepared by mixing the cyanine dye (A) and  
the diaryliodonium salt (B) with a polymerizable compound  
having an ethylenically unsaturated double bond (C)  
10 (polymerizable compound). The polymerizable compound is  
usually a compound having an ethylenically unsaturated bond  
by which an addition polymerization reaction occurs to cause  
curing. Typical examples of the polymerizable compounds are  
an unsaturated carboxylic acid, an ester of unsaturated  
15 carboxylic acids and polyhydroxy compounds, an addition  
product of unsaturated carboxylic acids and epoxides, and  
acrylamides or methacrylamides (hereinafter (meth)acrylamide)  
and the like. The polyhydroxy compounds include aliphatic or  
aromatic polyhydroxy compounds, and mixtures thereof. A  
20 polycarboxylic acid which does not have an unsaturated bond  
can be mixed with the unsaturated carboxylic acid. Examples  
of unsaturated carboxylic acids are acrylic acid,  
methacrylic acid, itaconic acid, maleic acid and the like.  
Examples of aliphatic polyhydroxy compounds are diols, e.g.  
25 ethylene glycol, diethylene glycol, triethylene glycol,  
tetraethylene glycol, neopentyl glycol, propylene glycol,

1,2-butanediol and the like; high alcohols, e.g. trimethylolethane, trimethylolpropane, pentaerythritol, tripentaerythritol and the like. Examples of aromatic polyhydroxy compounds are hydroquinone, resorcinol, catechol, pyrogallol and the like. Epoxides include

5 trimethylolpropane polyglycidyl ether, pentaerythritol polyglycidyl ether, propylene glycol diglycidyl ether, diglycidyl ester of phthalic acid, a reaction product of epichlorohydrin with 2,2-bis(4-hydroxyphenyl)-propane and the like. Typical examples of the (meth)acrylamides are

10 acrylamide, ethylenebisacrylamide, ethylenebismethacrylamide, hexamethylenebisacrylamide, hexamethylenebismethacrylamide and the like. Examples of polycarboxylic acids without an unsaturated bond are

phthalic acid, isophthalic acid, terephthalic acid,

15 tetrachlorophthalic acid, trimellitic acid, pyromellitic acid, benzophenone dicarboxylic acid, glutaric acid, adipic acid, sebacic acid, tetrahydrophthalic acid and the like.

Although the photopolymerizable composition containing the above three components (A), (B) and (C) of

20 the present invention has sufficient sensitivity, in order to make it more sensitive, it may also contain a compound (D) represented by the formula



wherein  $R_5$  represents a phenyl group or a substituted phenyl

25 group, and  $Z$  represents an oxygen atom, a sulfur atom or -NH-. Examples of the compounds (D) are phenoxy acetate, o-



chlorophenoxy acetate, thiophenoxy acetate, o-chlorothiophenoxy acetate, N-phenylglycine, N-(p-methoxyphenyl)glycine and the like.

The compound (A) employed in the present invention is present in the composition in an amount of 0.001 to 0.015  
5 mol, preferably 0.002 to 0.008 mol based on 100 g of the polymerizable compound (C). An amount of the diaryliodonium salt (B) is within the range of 0.003 to 0.05 mol, preferably 0.01 to 0.03 mol based on 100 g the polymerizable compound (C). The compound (D) is present in an amount of  
10 0.001 to 0.04 mol, preferably 0.003 to 0.02 mol based on 100 g of the polymerizable compound (C). Amounts less than the lower limit of each component cause the photosensitivity to deteriorate and curing the composition takes a long time. Amounts more than the upper limit of each component result  
15 in poor storage stability and a cured film having low film strength or low solvent resistance.

The photopolymerizable composition of the present invention may contain polymer binders, heat-polymerization inhibitors, plasticizers and coloring agents, if desired.  
20 The polymer binders can be those which improve miscibility, film-forming properties, developability, adhering properties and the like.

The composition of the present invention may be prepared by known methods. For example, the above components  
25 may be mixed in a cool and dark place using a high speed mixer. Mixing can be carried out in the presence

of a suitable solvent. Suitable solvents are ketones, e.g. methyl ethyl ketone, acetone and cyclohexanone; esters, e.g. ethyl acetate, butyl acetate, amyl acetate and ethyl propionate; aromatic hydrocarbons, e.g. toluene, xylene, benzene, monochlorobenzene; ethylene glycol monoalkyl ether, e.g. ethylene glycol monomethyl ether, ethylene glycol monoethyl ether and ethylene glycol monobutyl ether; alcohols, e.g. methanol, ethanol and propanol; ethers, e.g. tetrahydrofuran and dioxane; and the like.

A photosensitive layer of the composition of the present invention may be formed on a substrate by known methods. For example, it may be coated on the substrate using a bar-coater or a spinner and dried to form a photosensitive layer. The photosensitive layer is optionally subjected to a known treatment in order to prevent decline of sensitivity and storage stability due to oxygen. For example, the resin layer may be covered by a removable transparent sheet or provided with a coating of wax having low oxygen permeability or of a water-soluble or alkaline water-soluble polymer.

The photosensitive resin layer can be exposed to a light source generating light having a wavelength of more than 600 nm to cure. Examples of suitable light sources include a semiconductor laser, a helium-neon laser and the like. The photosensitive resin layer can also be exposed to a conventional light source containing ultraviolet or visible light, e.g. an argon laser, a helium-cadmium laser, a krypton laser, a high pressure mercury lamp, a ultrahigh

pressure mercury lamp, a moderate pressure mercury lamp and a metal halide lamp. Development after curing may be carried out by dissolving an uncured portion with a developing solution which can be selected depending on the type of photosensitive resin layer.

The composition of the present invention is very sensitive to light having a wavelength of 600 to 900 nm. The composition also has excellent storage stability over time.

EXAMPLES

The present invention is illustrated by the following examples, but they are not to be construed as limiting the present invention.

Examples 1 to 11 and Comparative Examples 1 to 6

Preparation of photopolymerizable composition

A first solution was prepared by dissolving 100 parts by weight of an acryl polymer having a weight average molecular weight of 48,000 and an acid value of 75 (available from BF Goodrich Company as Carboset\* XL-44) in 700 parts by weight of methyl ethyl ketone and then adding 100 parts by weight of pentaerythritol triacrylate.

Next, a second solution was prepared by dissolving the components A, B, C, D and E of Table 1 in a mixture of 300 parts by weight of ethyleneglycol monomethyl ether and 300 parts by weight of ethyl alcohol in amounts shown in Table 1. The second solution was mixed with the first solution to form a photosensitive solution. The components

\*Trade mark

D and E are compounds for comparison which are known to combine with the dye.

Preparation of a test panel

The solution was coated using a bar coater on an aluminum substrate in a dried amount of  $2 \text{ g/m}^2$  and dried at 5  $60^\circ\text{C}$  for 3 minutes to form a photosensitive layer having 2.0 micrometer. The photosensitive layer was then coated using the bar coater with a 5 % polyvinyl alcohol solution having a saponification degree of 88 % and a polymerization degree of 500 in a thickness of 2 micrometer to form an 10 overcoat layer.

Measurement of photosensitivity and stability over time

The obtained test panel was piled with Step Tablet No. 2 (21 steps) available from Kodak Company and irradiated 15 for 30 seconds with light of about 630 nm wavelength and  $2.0 \text{ mW/cm}^2$  light intensity from a 150 W xenone lamp available from Ushio Inc. through Toshiba\* Y-47 filter and Toshiba KL-63 filter available from Toshiba Corporation. Another piled panel was also irradiated for 30 seconds with light of 20 about 800 nm and 1.0 mW light intensity from the same 150 W xenone lamp through Toshiba Y-47 filter and Toshiba KL-80 filter. The irradiated panel was developed with a 1 wt% sodium carbonate solution. Exposure energy for curing was calculated as sensitivity based on the cured step number. 25 For storage stability over time, the uncured panel was

\*Trade Mark

stored in a dark place at 50°C for 50 days and subjected to the same sensitivity test. The results of the sensitivity and storage stability over time tests are shown in Table 1.

1338095

Example Nos.	Component (mmol) <sup>1)</sup>					Sensitivity <sup>2)</sup> (mJ/cm <sup>2</sup> )		Storage stability with time
	A	B	C	D	E	630 nm	800 nm	
1	A-1 3.0	B-1 2.0	-	-	-	9.0	-	No change
2	A-1 7.5	B-1 2.0	-	-	-	9.0	-	No change
3	A-2 7.5	B-1 2.0	-	-	-	2.0	-	No change
4	A-3 3.0	B-1 1.0	-	-	-	2.0	-	No change
5	A-3 3.0	B-1 2.0	-	-	-	1.4	-	No change
6	A-3 3.0	B-2 2.0	-	-	-	1.0	-	No change
7	A-3 3.0	B-1 2.0	1.0	-	-	0.7	-	No change
8	A-4 3.0	B-1 2.0	-	-	-	-	2.8	No change
9	A-4 3.0	B-2 2.0	-	-	-	-	2.0	No change
10	A-5 3.0	B-1 2.0	-	-	-	-	2.0	No change
11	A-5 3.0	B-1 2.0	1.0	-	-	-	1.4	No change
Comparative ex.								
1	A-1 3.0	-	-	1.3	-	9.0	-	*1
2	A-1 3.0	-	-	-	0.5	12.8	-	*2
3	A-3 3.0	-	-	1.3	-	1.4	-	*3
4	A-3 3.0	-	-	-	0.5	2.0	-	*2
5	A-5 3.0	-	-	1.3	-	-	2.0	*1
6	A-5 3.0	-	-	-	0.5	-	4.0	*2

1) Based on 100 g of pentaerythritol triacrylate.

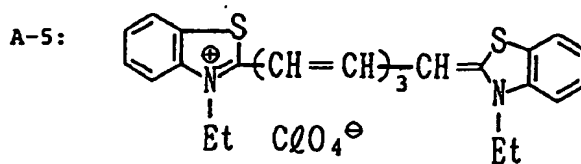
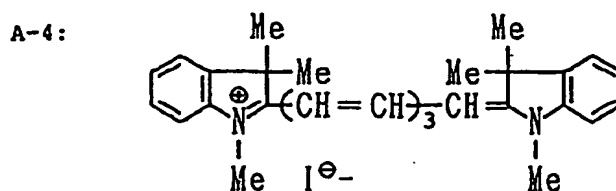
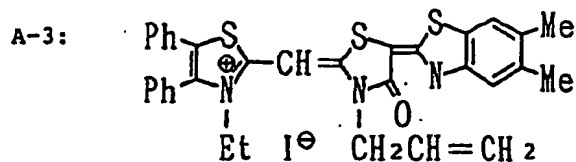
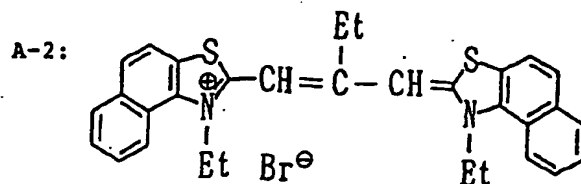
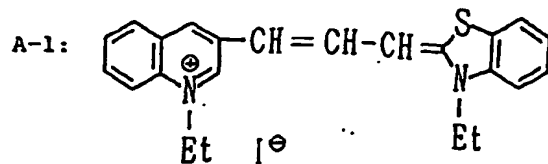
2) The smaller the higher sensitivity.

\*1 Sensitivity reduced to one-sixths after 14 days, and the photosensitive layer discolored.

\*2 The photosensitive layer was not soluble in the developing solution after 6 days, and the photosensitive layer discolored.

\*3 Sensitivity reduced to one-eighths after 13 days, and the photosensitive layer discolored.

1338095



B-1: Diphenyliodonium chloride

B-2: Diphenyliodonium tetrafluoroborate

C: N-Phenylglycine

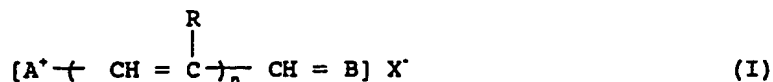
D: 2,4,6-tris(trichloromethyl)-1,3,5-triazine

E: 3,3',4,4'-tetra(t-butylperoxycarbonyl)-benzophenone

Claims:

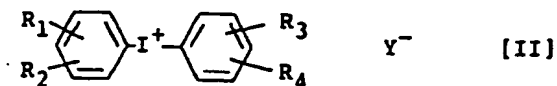
1. A photopolymerizable composition comprising a polymerizable compound having an ethylenically unsaturated double bond and a photopolymerization initiator wherein the photopolymerization initiator comprises;

(A) a cyanine dye having a peak absorption wavelength within 550 to 850 nm, represented by the formula;



wherein A and B respectively represent a substituted or unsubstituted nitrogen-containing heterocyclic ring the substituents being selected from the group consisting of a C<sub>1</sub>-C<sub>3</sub> alkyl group, a C<sub>1</sub>-C<sub>3</sub> alkenyl group, a phenyl group, a hydroxyl group, an amino group, a dialkyl(C<sub>1</sub>-C<sub>3</sub>)amino group, a carboxyalkyl(C<sub>1</sub>-C<sub>3</sub>) group, a sulphoalkyl(C<sub>1</sub>-C<sub>3</sub>) group and a C<sub>3</sub>-C<sub>6</sub> esteralkyl group and the nitrogen atom in the A ring has a positive charge, X<sup>-</sup> is a counter anion, R represents a hydrogen atom, an alkyl group having 1 to 3 carbon atoms, a phenyl group and a halogen atom, and n is an integer of 0 to 3; and

(B) a diaryliodonium salt of the formula [II];



wherein R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> respectively represent a hydrogen atom, a halogen atom, a C<sub>1</sub>-C<sub>4</sub> alkyl group, a C<sub>1</sub>-C<sub>4</sub> alkoxy group or a nitro group, and Y<sup>-</sup> represents a halogen ion, a hydroxyl ion, HSO<sub>4</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, AsF<sub>6</sub><sup>-</sup> or SbF<sub>6</sub><sup>-</sup>, wherein said

**B**



15

1338095

compound (A) is present in an amount of 0.001 to 0.015 mol and said diaryliodonium salt (B) is present in an amount of 0.003 to 0.05 mol, the amounts being based on 100 g of the polymerizable compound.

- 5                    2.    The composition according to claim 1 further comprising a compound represented by the formula



wherein  $R_3$  represents a phenyl group or a phenyl group substituted with chlorine, a  $C_1-C_4$  alkoxy group or a  $C_1-C_4$  alkyl group, and Z represents an oxygen atom, a sulfur atom or -NH-  
10                    wherein the compound (III) is present in an amount of 0.001 to 0.04 mol based on 100 g of the polymerizable compound.



B